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(54) Abstract Title
Broadband reflective polarizer

(57) The invention relates to a broadband reflective polarizer that comprises a layer of a polymerized mesogenic material exhibiting a helically twisted molecular structure with planar alignment, said reflective polarizer being obtainable or obtained by a process wherein a thermochromic polymerizable mesogenic material comprising a mixture of

- a) at least one achiral polymerizable mesogenic compound,
- b) at least one chiral compound that can in addition be polymerizable and/or mesogenic,
- c) a polymerization initiator,
- d) optionally a dye component,

is coated on a substrate or between two substrates in the form of a layer, aligned in a planar orientation so that the axis of the molecular helix extends transversely to the layer, and polymerized by exposure to heat or actinic radiation, and optionally the substrates being removed from the polymerized material, in which the temperature is varied during polymerization of the layer of polymerizable material. The invention further relates to a process of preparing such a broadband reflective polarizer and to a liquid crystal display comprising such a broadband reflective polarizer.

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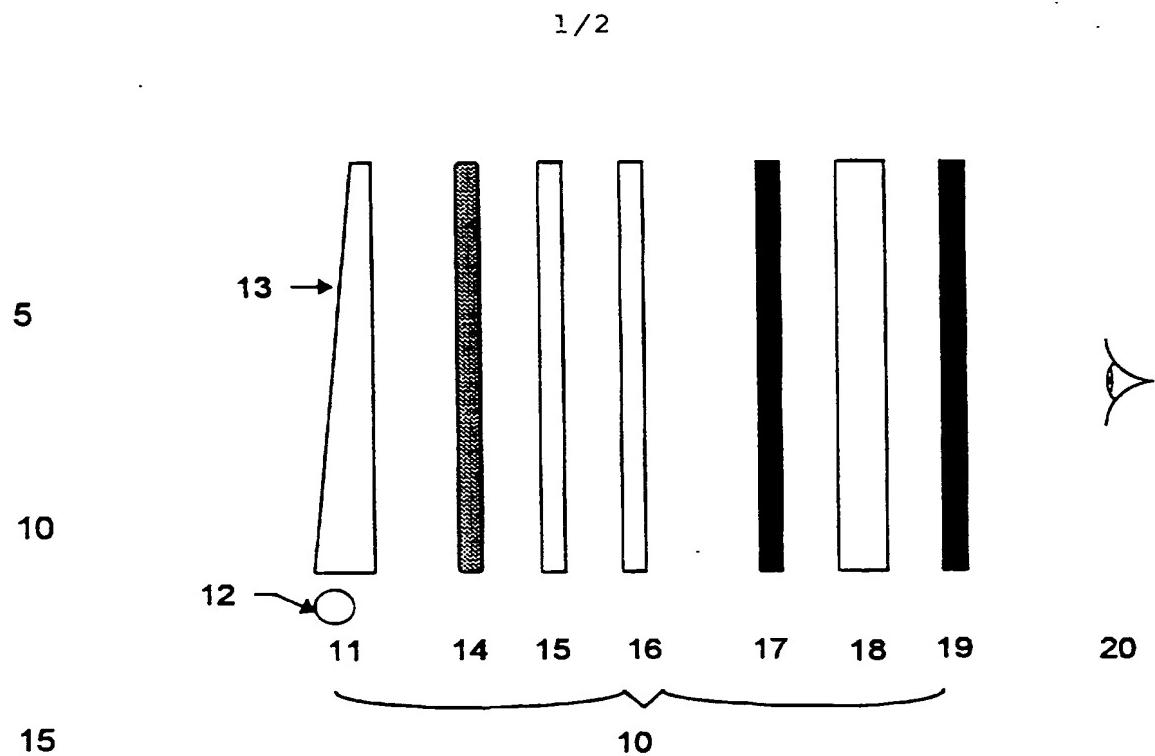


Figure 1

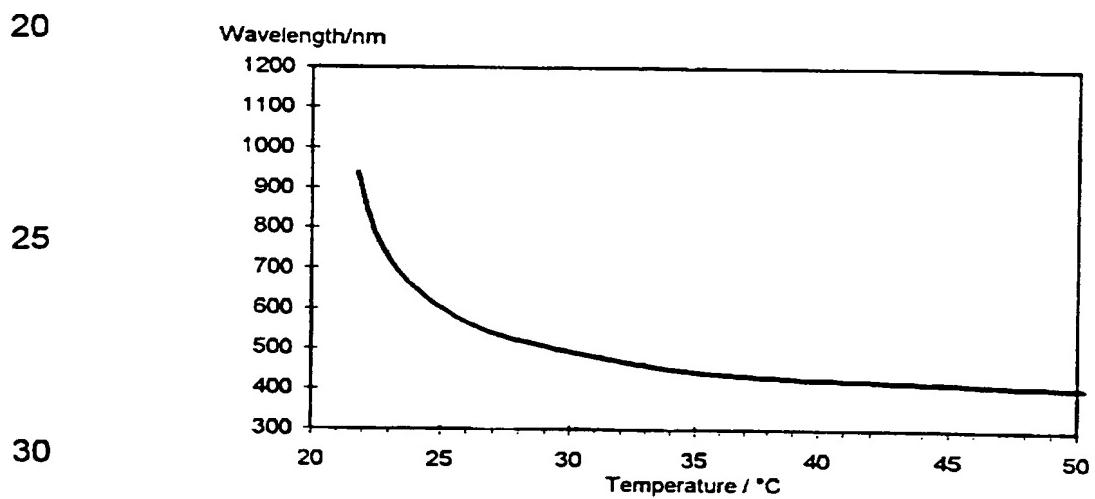
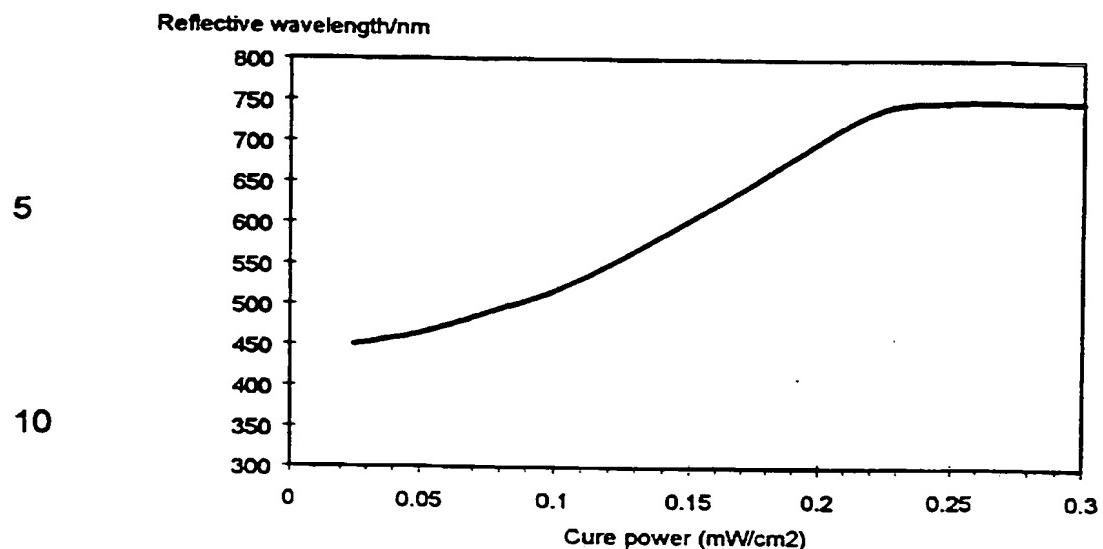
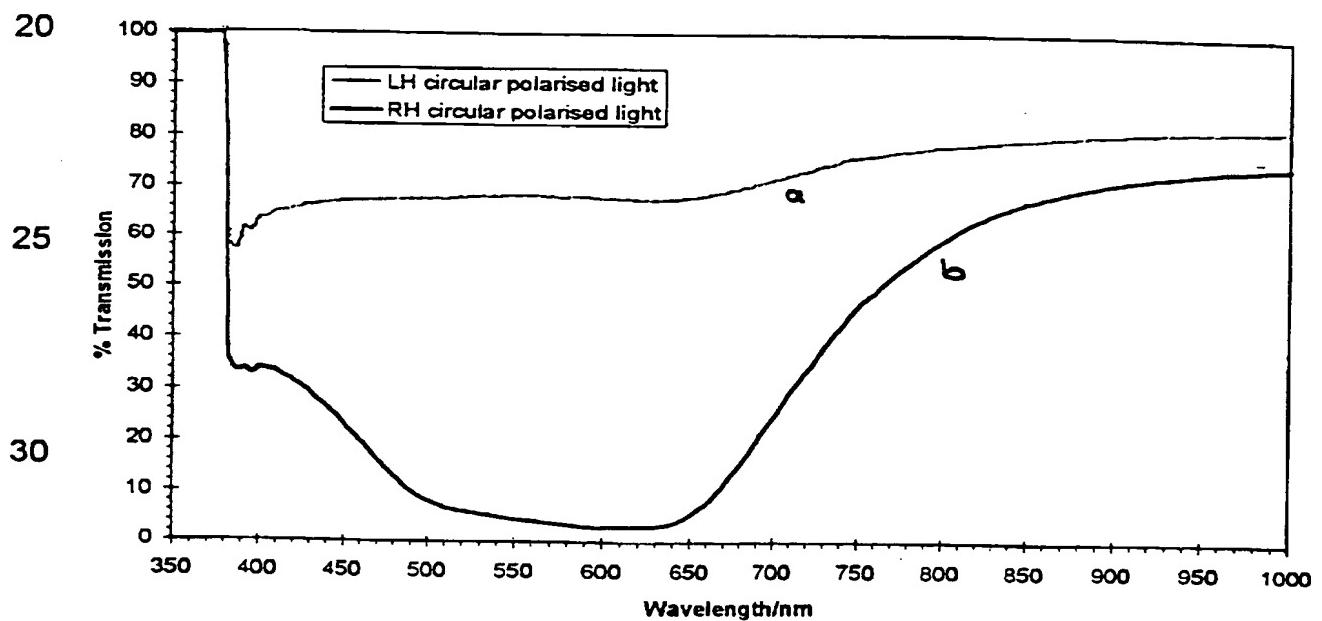


Figure 2

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**Figure 3**

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Figure 4

Broadband Reflective Polarizer

The invention relates to a broadband reflective polarizer comprising a layer of a polymerized mesogenic material exhibiting a helically twisted molecular structure with planar alignment, said reflective polarizer being obtainable by a process wherein a mixture of a thermochromic polymerizable mesogenic material comprising

5 a) at least one achiral polymerizable mesogenic compound,

10 b) at least one chiral compound that can in addition be polymerizable and/or mesogenic,

 c) a polymerization initiator,

 d) optionally a dye component,

15 is coated on a substrate or between two substrates in form of a layer, aligned in a planar orientation so that the axis of the molecular helix extends transversely to the layer, and polymerized by exposure to heat or actinic radiation, and optionally the substrates are removed from the polymerized material, characterized in that the temperature

20 varied during polymerization of said thermochromic polymerizable mesogenic material.

The invention further relates to a process of preparing such a broadband reflective polarizer and to a liquid crystal display comprising such a broadband reflective polarizer.

25 Figure 1 shows a display device according to an exemplary embodiment of the present invention.

30 Figure 2 shows the change of the reflective wavelength versus the temperature of a thermochromic polymerizable mixture according to example 1 of the present invention.

35 Figure 3 shows the reflective wavelength of reflective polarizers according to example 2 versus the curing power.

Figure 4 shows the transmission spectrum of a broadband reflective polarizer according to example 3, with (a) indicating the transmitted and (b) the reflected light.

- 5 Liquid crystal displays of the state of the art often show a reduced brightness due to light absorption in the optical path, which is in particular caused by the linear polarizers that are used in displays. For example, in backlit displays these linear polarizers can absorb more than 60% of the light intensity emitted from the backlight.
- 10 Therefore, circular polarizers - also known as "reflective polarizers" - have been developed that can very efficiently convert unpolarized light into polarized light. They usually comprise a layer of a chiral liquid crystalline material, like e.g. a cholesteric liquid crystal, that exhibits a helically twisted molecular structure and further exhibits planar alignment, i.e. wherein the axes of the molecular helices are oriented substantially perpendicular to the plane of the layer.
- 15
- 20 If unpolarized light is incident on such a circular polarizer, 50% of the light intensity are reflected as circularly polarized light with the same twist sense as that of the molecular helix, whereas the other 50% are transmitted. The reflected light is depolarized (or its sense of polarization is reversed) in the backlight of the display, and is redirected onto the polarizer. In this manner theoretically 100% of a given waveband of the unpolarized light incident on the circular polarizer can be converted into circularly polarized light.
- 25
- 30 The circularly polarized light can be converted into linear polarized light by means of a quarter wave optical retarder and optionally also a compensation film.
- 35 The bandwidth $\Delta\lambda$ of the waveband reflected by a circular polarizer as described above is depending on the birefringence of the mesogenic material Δn and the pitch of the molecular helix p according to the equation $\Delta\lambda = \Delta n \times p$. Thus, the bandwidth is limited by the birefringence of the material. However, for an application in liquid

crystal displays it is desirable that the bandwidth of the polarizer should comprise a substantial portion of the visible wavelength range.

- Recently reflective polarizers have been developed that reflect a wider waveband of incident light. These polarizers comprise a liquid crystalline material with a helically twisted structure and a planar orientation, and are further characterized in that the pitch of the molecular helix is varying in a direction normal to the layer, which leads to a large bandwidth of the reflected wavelength band.
- 5 The European Patent Application EP 0 606 940 discloses a circular reflective polarizer with a bandwidth of up to 400 nm that consists of a film of a polymerized cholesteric liquid crystal.
- 10 Such a broadband reflective polarizer, when being used in combination with a quarter wave foil and optionally also a compensation film in a liquid crystal display, can give an increased brightness of up to 60 - 70 % at normal viewing incidence.
- 15 At larger viewing angles, however, the luminance of a display with a broadband reflective polarizer is decreasing, and normally falls below the luminance of a display with a conventional linear polarizer (usually a dichroic polarizer) at some angle within a 60° viewing cone. The angle at which this occurs in the horizontal viewing plane is called the cross-over angle. For a broadband cholesteric polarizer with a high brightness gain this usually occurs at a maximum of around 50° when a compensator film is used.
- 20 Furthermore, at large viewing angles often an undesired colour shift of the light transmitted by such a broadband reflective polarizer is observed.
- 25 It is therefore an aim of the present invention to provide a broadband reflective polarizer that shows improved optical properties at large viewing angles, in particular an improved off-axis brightness, and also exhibits a large bandwidth comprising a substantial portion of
- 30
- 35

the visible spectrum of light, and in the ideal case covering the whole visible spectrum. Another aim is to provide a liquid crystal display device comprising such a polarizer.

5 The broad bandwidth of a reflective polarizer film as described in the EP 0606 940 is caused by a gradient of the helical pitch in the film. This pitch gradient is reported in the EP 0606 940 to be achieved by the process of preparing the polarizer, said process comprising the polymerization of a mixture containing achiral compounds with one 10 polymerizable group and chiral compounds with two polymerizable groups. As these compounds show different reactivity towards the polymerization reaction, corresponding to the different number of polymerizable groups, a diffusion process is said to take place during polymerization. This diffusion is reported to lead to a concentration 15 gradient of chiral versus achiral compounds, and thereby to a pitch gradient. A more detailed explanation of this process can be found in the EP 0 606 940.

20 However, the diffusion process as reported in the EP 0606 940 can take many minutes, and limits the production speed of a polarizer using this technique.

25 Furthermore, the process of preparing a broadband reflective polarizer film in the EP 0 606 940 is described only for glass substrates. However, a process comprising the use of glass substrates is convenient only if small samples are produced. For the preparation of large area films, in particular for mass production glass substrates are highly unsuitable. Furthermore, from the disclosure of the EP 0606 940 it is not clear if such a complex process of achieving a broad 30 bandwidth also works on other substrates than glass.

35 Thus, another aim of the invention is to provide a method of manufacturing a broadband reflective polarizer in an efficient and cost-effective manner which is in particular suitable for mass production. Other aims of the invention are immediately evident to a person skilled in the art from the following description.

- 5 The inventors have developed a technique that allows the preparation
of a broadband reflective polarizer on plastic substrates and is also
suitable for mass production. This method comprises the steps of
coating a polymerizable liquid crystalline material with a chiral phase
on a substrate or between two substrates in form of a thin layer,
aligning the material into a planar orientation and polymerizing the
material to freeze in the helically twisted, planar liquid crystalline
phase structure.
- 10 The inventors also have found that the optical properties of a
broadband reflective polarizer prepared by this process are very
sensitive to the method of production of the polarizer. In particular, it
was found that the off-axis brightness of such a polarizer can be
improved if a thermochromic polymerizable mesogenic material is
used in the process as described above and the temperature is
altered during polymerization.
- 15 Thermochromic materials are characterized in that they show a
change of the reflective wavelength upon temperature variation.
Thermochromic compositions are disclosed for example in the
international application WO 90/02161.
- 20 Furthermore, thermochromic polymerizable compositions are
described in the British Application GB 2,315,760, the entire
disclosure of which is introduced into this application by way of
reference.
- 25 Thus, it has been found that the above mentioned aims can be
achieved and the drawbacks of prior art can be overcome with a
broadband reflective polarizer that is obtainable by a process as
described in the following.
- 30 A broadband reflective polarizer prepared by a process according to
the present invention is in particular advantageous in that, when
used in a liquid crystal display, it exhibits a high luminance and a
- 35

considerable brightness gain compared to a conventional linear polarizer (such as e.g. a dichroic polarizer) up to large viewing angles. In some cases, when using an inventive broadband reflective polarizer even no cross-over angle can be observed at all over the whole range of measured viewing angles. Furthermore, an inventive broadband reflective polarizer exhibits a high temperature stability of the mechanical and optical properties.

One of the objects of the present invention is a broadband reflective polarizer comprising a layer of a polymerized mesogenic material exhibiting a helically twisted molecular structure with planar alignment, said reflective polarizer being obtainable by a process wherein a mixture of a thermochromic polymerizable mesogenic material comprising

- 15 a) at least one achiral polymerizable mesogenic compound,
- b) at least one chiral compound that can in addition be polymerizable and/or mesogenic,
- c) a polymerization initiator,
- 20 d) optionally a dye component,

is coated on a substrate or between two substrates in form of a layer, aligned in a planar orientation so that the axis of the molecular helix extends transversely to the layer, and polymerized by exposure to heat or actinic radiation, and optionally the substrates are removed from the polymerized material, characterized in that the temperature is being varied during polymerization of said thermochromic polymerizable mesogenic material.

30 Another object of the invention is a process of preparing a broadband reflective polarizer as described in the foregoing and the following.

Another object the invention is a liquid crystal display comprising a liquid crystal cell and a reflective polarizer as described in the foregoing and the following, and optionally further comprising at least 35 one of the following components

- 1) an optical retardation film with a retardation which is approximately 0.25 times the wavelength of the band reflected by the reflective polarizer,
- 5 II) a linear polarizer,
- III) a compensation film comprising a layer of an anisotropic polymer material with a homeotropic or tilted homeotropic orientation.
- 10 Preferred embodiments of the invention relate to
- a broadband reflective polarizer obtainable by a process as described above, wherein the temperature is varied continuously between a minimum and a maximum value during polymerization of the thermochromic polymerizable mesogenic material.
 - A broadband reflective polarizer obtainable by a process as described above, wherein at least one of said substrates is a plastic film.
 - A broadband reflective polarizer obtainable by a process as described above, wherein the thermochromic polymerizable mesogenic mixture comprises a dye component d) absorbing the actinic radiation used for polymerization.
 - A broadband reflective polarizer obtainable by a process as described above, the reflection characteristics of which, like the central wavelength, the shape or the bandwidth of the reflected spectrum and the viewing angle dependence of these reflection characteristics, are controlled by varying the temperature during polymerization of the thermochromic polymerizable mesogenic material.
 - A broadband reflective polarizer with a reflection bandwidth of at least 200 nm.
 - A broadband reflective polarizer wherein the pitch of the molecular helix varies asymmetrically in a direction normal to the plane of the polarizer.
- 20
- 25
- 30
- 35

- A broadband reflective polarizer film with an asymmetrical pitch structure, wherein the pitch of the molecular helix substantially increases in a direction normal to the film plane from a smaller value at one side of the film to a higher value at the opposite side of the film.
- A broadband reflective polarizer obtainable by a process as described above, wherein the polymerized material forms a three-dimensional network.
- A broadband reflective polarizer obtainable by a process as described above, wherein the thermochromic polymerizable mesogenic material contains at least one chiral polymerizable mesogenic compound having one polymerizable group and at least one achiral polymerizable mesogenic compound having one polymerizable group.
- A broadband reflective polarizer obtainable by a process as described above, wherein the thermochromic polymerizable mesogenic material contains at least one chiral polymerizable mesogenic compound having one polymerizable group and at least one achiral polymerizable mesogenic compound having two or more polymerizable groups.
- A broadband reflective polarizer obtainable by a process as described above, wherein the thermochromic polymerizable mesogenic material contains at least one non-polymerizable chiral compound and at least one achiral polymerizable mesogenic compound having one or two polymerizable groups.
- A liquid crystal display device comprising the optical elements I, II and optionally also III as described above, wherein the linear polarizer is preferably situated in the optical path between the reflective polarizer and the liquid crystal cell.
- A liquid crystal display device comprising the optical elements I, II and optionally also III as described above, wherein the angle between the optical axis of the linear polarizer II and the major optical axis of the optical retardation film I is from 30 degrees to 60 degrees.

- The preparation of a broadband reflective polarizer according to the present invention is achieved by polymerization of a layer of a thermochromic polymerizable mesogenic material exhibiting a helically twisted molecular structure and planar alignment, together with controlled variation of the temperature during polymerization. Thereby the helical pitch and the reflective wavelength in the layer are altered during polymerization.
- At the same time, the polymerization is graduated throughout the thickness of the layer by different absorption of the actinic radiation that starts the polymerization reaction in the layer. The difference of absorption leads to a different speed of polymerization, and can be further enhanced by adding a dye to the polymerizable material that absorbs the actinic radiation used for polymerization. In some cases, however, the different absorption of actinic radiation of a polymerizable mixture comprising components a) to c) above is already sufficient to establish a graduated polymerization, and a dye is not needed.
- The combination of graduated polymerization and temperature variation as described above leads to the creation of a pitch gradient throughout the thickness of the layer that is fixed upon polymerization, and thus to a polymer film that exhibits different reflective wavelengths at different points within the film thickness.
- Preferably the speed of temperature variation is as high as possible, in order to allow rapid production of the polymer film, and is limited only by the speed at which the temperature change is transferred to the polymerizable mixture and then how rapidly the molecular helix can wind up or unwind to give the desired change of the helical pitch.
- In a preferred embodiment of the present invention, the thermochromic polymerizable mixture is heated, preferably at a constant rate, from a minimum temperature to a maximum temperature when being polymerized. At another preferred

embodiment, the thermochromic polymerizable mixture is heated or cooled brought to a temperature within the chiral mesophase range of the mixture before starting the polymerization, and is then further heated to a specific temperature within the chiral mesophase during
5 polymerization.

If for example the polymerization is completed first in the region close to one surface of the layer of the thermochromic polymerizable material, and completed later in the region close to the opposite
10 surface of the layer, an asymmetrical pitch gradient throughout the resulting polymer film is obtained.

Broadband reflective polarizer films according to the present invention are preferred that have an asymmetrical pitch gradient in
15 the direction normal to the plane of the film. These polarizers, when used in a liquid crystal display, give particularly high brightness at large viewing angles.

The term viewing angle as referred to in connection with an optical
20 film or a combination of optical films, such as compensation or polarizer films, according to the present invention in the foregoing and the following is to be understood as the angle of observation relative to the normal of the plane of the film under which for example
25 the contrast, the brightness and/or the colour shift of the film is characterized by an acceptable level for the envisaged application.

It should also be pointed out that the method according to this invention does not necessarily require the use of chiral and achiral polymerizable compounds having different reactivity. For example, it
30 is also possible to use a polymerizable mixture comprising only monoreactive chiral and achiral compounds (i.e. compounds having one polymerizable group), or a mixture comprising non-polymerizable chiral compounds, like e.g. chiral dopants. As these compounds are often cheaper and easier to prepare than mono- or
35 direactive polymerizable chiral compounds, this is a considerable advantage over prior art.

However, special preferred embodiments of the present invention also relate to the use of polymerizable chiral compounds.

5 The waveband reflected by the inventive broadband reflective polarizer ideally covers the whole visible spectrum, and is preferably within a wavelength range from 400 to 900 nm. For most applications, a reflected waveband within a range from 450 to 800 nm is acceptable. In specific embodiments, a reflected waveband
10 within a range from 480 to 700 nm is still suitable.

15 The bandwidth of the wavelength band is preferably larger than 200 nm, particularly preferably larger than 300 nm, very particularly preferably larger than 400 nm.

20 The transmission versus wavelength curve of the transmission spectrum of a broadband reflective polarizer according to the present invention (as depicted, for example, in Figure 4) can be of symmetric or asymmetric shape. It can be unimodal, bimodal or exhibit a multiple peak distribution, which means that it can show one, two or more than two local maxima of reflection.

25 A preferred embodiment of the present invention is characterized in that the spectrum has an unimodal peak distribution.

30 A broadband reflective polarizer film according to the present invention is characterized in that the helical pitch of the helically twisted molecular structure varies in a direction normal to the plane of the layer. This variation can be symmetrical, with the pitch increasing from a minimum value - or decreasing from a maximum value - in the middle of the layer towards the outer edges of the film, or it can be asymmetrical, with the pitch substantially increasing from a smaller value at one edge of the film to a higher value at the opposite edge of the film.

35

Preferably the inventive reflective polarizer exhibits an asymmetrical structure of the helical pitch, with the pitch substantially increasing from a smaller, preferably a minimum, value at one edge of the film to a higher, preferably a maximum, value at the opposite edge of the film, when looking in the direction normal to the layer.

In order to create linear polarized light, e.g. when used in a liquid crystal display, an inventive reflective polarizer is preferably used in combination with an optical retardation film. The optical retardation film comprises a layer of a birefringent material selected such that its optical retardation is approximately 0.25 times the wavelength of the centre of the bandwidth reflected by the broadband reflective polarizer. As a result, this retarder serves as a quarter wave plate or foil (QWF) which converts circular polarized light into linear polarized light.

As a QWF for example a stretched plastic film, such as stretched PET, PVA, PC or TAC can be used. It is also possible to use a layer of an oriented polymerized liquid crystalline material.

The QWF may be connected to the reflective polarizer as a separate optical element. Preferably, the reflective polarizer and the QWF are integrated so that they form an individual optical element. This can be done for example by laminating the QWF and the reflective polarizer together after manufacturing the polarizer.

In another preferred embodiment the thermochromic polymerizable mesogenic material is coated and cured directly on a QWF which serves as a substrate, thus simplifying the production process.

When a single QWF is used together with the reflective polarizer, its retardation typically increases with decreasing wavelength, since the birefringence will increase towards lower wavelengths. This spread of the birefringence, which is known as dispersion, is low for some materials, like e.g. PVA, but higher for other materials, like e.g. PC and PET. This leads to a mismatch between retardation of the QWF

and the wavelengths reflected by the reflective polarizer. As a result, the conversion from circularly polarized light into linearly polarized light is not optimal over the entire bandwidth of the polarizer. This can be a disadvantage in particular for broadband polarizers.

5

Therefore in another preferred embodiment an inventive liquid crystal display device comprises a combination of two or more optical retardation layers, the retardation of these layers being selected in such a manner that due to the difference in retardation of the layers the nett retardation of the combination is approximately 0.25 times the wavelength of the light reflected by the polarizer over a substantial portion of the reflected bandwidth of the polarizer. This combination of layers is then used as a QWF together with the inventive reflective polarizer.

10

In another preferred embodiment the inventive reflective polarizer and the QWF are used together with a compensation film in order to compensate the viewing angle dependence of the phase retardation of light transmitted by the reflective polarizer and/or the QWF. The compensation film can be positioned adjacent to either side of the QWF.

15

Preferably a compensation film is used of which the phase retardation is opposite in sign and substantially equal in magnitude to the phase retardation of the reflective polarizer over a wide range of viewing angles.

20

Particularly preferably a compensation film is used that comprises a layer of an anisotropic polymer material with a homeotropic or tilted homeotropic orientation.

25

The light incident on the reflective polarizer is tranformed into circularly polarized light. However, this applies only to light with a wavelength corresponding to the bandwidth of the polarizer, and to light at normal incidence, i.e. parallel to the axis of the molecular helix, whereas, for example, light passing through the reflective polarizer at an angle to the normal will become elliptically polarized.

30

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This light will not be transformed completely by the QWF into linear polarized light of a single plane of polarization.

Especially when using the inventive reflective polarizer for the illumination of a liquid crystal display cell, this elliptically polarized component of light can lead to undesired reduction of the contrast of the display. Therefore in a preferred embodiment of the present invention a linear polarizer is provided in the optical path of the display after the QWF in order to cut off the component of light emitting from the reflective polarizer which is not ideally circularly polarized.

The linear polarizer disclosed above is preferably provided such that the angle between its optical axis and the major optical axis of the QWF is ranging from 30 to 60 degrees, especially preferably between 40 and 50 degrees.

The inventive reflective polarizer and liquid crystal display can additionally comprise other film or sheet components such as diffusers, adhesive layers, protective or release layers.

The function of the inventive reflective polarizer is further explained by **Figure 1**, which illustrates an exemplary embodiment of the invention. The main direction of light following the optical path is from the left side to the right side. The figure shows a display device 10 with a side-lit backlight unit 11 with a lamp 12 and a combined light guide and reflector 13, an inventive reflective polarizer 14, a QWF 15, a compensation film comprising a layer of a homeotropically aligned polymerized liquid crystalline material 16, and a linear polarizer 17. The figure further depicts a liquid crystal cell 18 and a second linear polarizer 19 behind the display cell.

Light emitted from the backlight 11 is interacting in a substantial part with the reflective polarizer 14. Half of the intensity of the interacted light is transmitted as right-handed or left-handed circular polarized light respectively, whereas the other half is reflected as circular polarized light of the opposite handedness. The reflected light is

5 redirected by the reflector 13 onto the reflective polarizer 14. The main part of the transmitted component is converted by the QWF 15 and the compensation film 16 into linear polarized light. Light which is not ideally linear polarized, such as elliptically polarized light, is cut off by the linear polarizer 17. The linear polarized light then passes through the display 18 and the second linear polarizer 19 to reach the viewer 20.

10 The brightness gain when using a broadband reflective polarizer according to the present invention instead of a conventional linear polarizer in a liquid crystal display is preferably at least 50 % or higher, in particular preferably at least 70 % or higher .

15 The brightness gain in this connection is defined as $I_a/I_b - 1$, wherein I_a is the intensity of light which is transmitted after passing through an assembly, consisting of an LCD backlight, an inventive reflective polarizer, a QWF, a compensation film and a linear polarizer, and

20 I_b is the intensity of light transmitted by an assembly consisting only of the backlight and the linear polarizer of the setup described above.

25 The brightness gain is depending on the efficiency of the light source to re-reflect rays of light. The preferred value given above relates to an efficient light source such as a conventional side-lit or meander backlight.

30 The measured brightness gain also depends on the sample size of the reflective polarizer covering the entire area of the backlight. If the backlight is only partially covered, the brightness gain decreases due to some of the light that is reflected back from the polarizer subsequently escaping from the system.

35 The cross over angle of a display comprising an inventive broadband reflective polarizer is preferably at least 40 °, particularly preferably at

at least 50 °. Preferably no cross over angle is observed within a 60 ° cone of viewing angles.

- 5 The colour difference (ΔE^*_{uv} in the CIE 1976 L*u*v* colour space) of a display comprising an inventive reflective broadband polarizer is preferably lower than that of a display that comprises a state of the art broadband polarizer for viewing angles from 0 ° to 90 °, i.e. for all possible viewing angles.
- 10 Apart from backlit displays, the reflective polarizer and the polarizer combination according to the present invention can also be applied in a reflective display, which instead of an electric light source makes use of a reflector that reflects light generated outside the display. The invention thus also relates to a reflective liquid crystal display device comprising an inventive reflective polarizer.
- 15

20 The thermochromic polymerizable mesogenic material used in the inventive process can comprise polymerizable compounds with one polymerizable group (monofunctional) and compounds with two or more polymerizable groups (di- or multifunctional). By varying the concentration of monofunctional and di- or multifunctional polymerizable compounds the crosslink density of the polymer film and thereby its physical and chemical properties such as the glass transition temperature, which is also important for the temperature dependence of the optical properties of the polarizer, the thermal and mechanical stability or the solvent resistance can be tuned easily.

25

30 The polymerizable mixture used for preparation of the inventive polarizer comprises at least one achiral and at least one chiral compound. By changing the ratio of chiral and achiral compounds the pitch lengths and thus the central wavelength of the reflected wavelength band of the polarizer can be varied. Preferably the ratio of the chiral and achiral mesogenic compound is selected so that the reflected spectrum is covering a substantial part of the spectrum of visible light.

35

The terms polymerizable mesogen, polymerizable mesogenic compound or polymerizable liquid crystal or liquid crystalline compound as used in the foregoing and the following comprise compounds with a rod-shaped, board-shaped or disk-shaped mesogenic group (i.e. a group with the ability to induce mesophase behaviour in a compound comprising such a group). These compounds do not necessarily have to exhibit mesophase behaviour by themselves. In a preferred embodiment of the present invention they show mesophase behaviour only upon admixture with other compounds or upon polymerization of the polymerizable mesogenic compounds or the mixtures comprising them.

Preferably the polymerizable mesogenic compounds exhibit mesophase behaviour on their own.

The term "mesogeneity supporting group" as used in the foregoing and the following is indicating a rod-shaped, board-shaped or disk-shaped group, which does not necessarily have to show mesogenic behaviour (i.e. the ability to induce mesophase behaviour in a compound comprising such a group) alone. It is also possible that such a group shows mesogenic behaviour if being combined in a compound with other groups, or if the compound comprising the mesogeneity supporting group is polymerized or admixed with other compounds comprising the same or other mesogenic or mesogeneity supporting groups.

The achiral polymerizable mesogenic compounds of component a) are preferably selected of formula I

P-(Sp-X)_n-MG-R I

wherein

P is $\text{CH}_2=\text{CW}-\text{COO}-$, $\text{WCH}=\text{CH}-\text{O}-$, $\text{WHC}\begin{array}{c} \diagdown \\ \text{O} \\ \diagup \end{array}\text{CH}-$ or
 $\text{CH}_2=\text{CH}-\text{Phenyl}-(\text{O})_k-$ with W being H, CH_3 or Cl and k being 0 or 1,

Sp is a spacer group having 1 to 20 C atoms,

X is a group selected from -O-, -S-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S- or a single bond,

5

n is 0 or 1,

R is an achiral alkyl radical with up to 25 C atoms which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S- or -C≡C- in such a manner that oxygen atoms are not linked directly to one another, or alternatively R is halogen, cyano or has independently one of the meanings given for P-(Sp-X)_n-, and

MG is a mesogenic or mesogeneity supporting group preferably selected of formula II

20

-(A¹-Z)_m-A²- II

wherein

25

Z is in each case independently -COO-, -OCO-, -CH₂CH₂-, -OCH₂-, -CH₂O-, -CH=CH-, -CH=CH-COO-, -OCO-CH=CH-, -C≡C- or a single bond,

30

A¹ and A² are each independently 1,4-phenylene in which, in addition, one or more CH groups may be replaced by N, 1,4-cyclohexylene in which, in addition, one or two non-adjacent CH₂ groups may be replaced by O and/or S, 1,4-cyclohexenylene, or naphthalene-2,6-diyl, it being possible for all these groups to be unsubstituted, mono- or polysubstituted with halogen, cyano or nitro groups or alkyl, alkoxy or alkanoyl groups having 1 to 7 C atoms wherein one or more H atoms may be substituted by F or Cl, and

35

m is 1, 2 or 3.

- As for the chiral compounds of component b), in principal all
 5 compounds can be used that are known to the skilled in the art for this purpose. Typical compounds are e.g. the commercially available chiral dopants S 1011, R 811 or CB 15 (Merck KGaA, Darmstadt, Germany).
- In a preferred embodiment of the present invention, component b) of
 10 the chiral polymerizable mesogenic material is essentially consisting of polymerizable chiral compounds, preferably polymerizable chiral mesogenic compounds.
- The polymerizable chiral compounds are preferably selected of
 15 formula III
- P-(Sp^{*}-X)_n-MG^{*}-R^{*} III
- wherein P, Sp^{*}, X and n have the meanings given for formula I,
 20 Sp^{*} is a spacer group having 1 to 20 C atoms,
- MG^{*} is a mesogenic or mesogenity supporting group, which is
 25 preferably selected of formula II given above, and
- R^{*} is H or an alkyl radical with up to 25 C atoms which may be
 unsubstituted, mono- or polysubstituted by halogen or CN, it
 being also possible for one or more non-adjacent CH₂ groups to
 be replaced, in each case independently from one another, by
 30 -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-,
 -CO-S- or -C≡C- in such a manner that oxygen atoms are not
 linked directly to one another, or alternatively R^{*} is halogen, cyano
 or has independently one of the meanings given for P-(Sp^{*}-X)_n,
- 35 with at least one of Sp^{*}, MG^{*} and R^{*} comprising a chiral structure element.

Particularly preferred are polymerizable mixtures comprising at least two polymerizable mesogenic compounds at least one of which is a compound of formula I.

5

In another preferred embodiment of the invention the achiral polymerizable mesogenic compounds are selected according to formula I, wherein R has one of the meanings of P-(Sp-X)_n- as given above.

10

Of the compounds of formula I and III especially preferred are those in which R and R* are F, Cl, cyano, or optionally halogenated alkyl or alkoxy, or has the meaning given for P-(Sp-X)_n- or P-(Sp*-X)_n- respectively. Further preferred are compounds wherein MG and MG* are of formula II with Z¹ and Z² being each independently -COO-, -OCO-, -CH₂-CH₂-, -CH=CH-COO-, -OCO-CH=CH- or a single bond.

15

Of the mesogenic groups wherein A¹ and/or A² denote a heterocyclic group, those containing a pyridine-2,5-diyl group, pyrimidine-2,5-diyl group or 1,3-dioxane-2,5-diyl group are particularly preferred.

20

Of the preferred mesogenic groups containing a substituted 1,4-phenylene group very particularly preferred are those substituted by F, Cl or an optionally fluorinated alkyl, alkoxy or alkanoyl group with 1 to 4 C atoms.

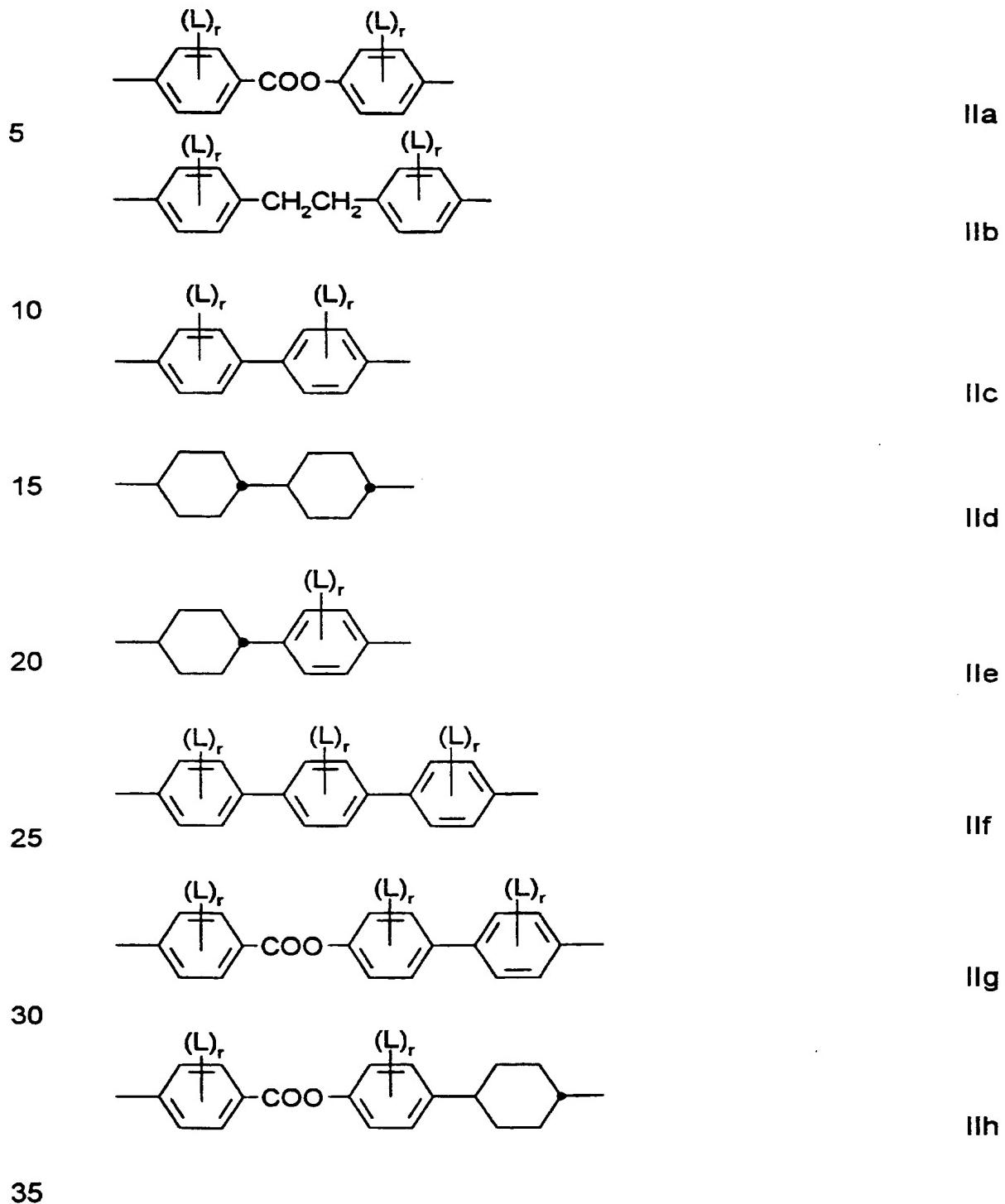
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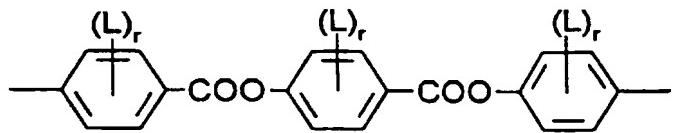
A smaller group of particularly preferred mesogenic groups of the formula II is listed below. For reasons of simplicity, in these formulae PheL is 1,4-phenylene, which is substituted in 2- and/or 3-position with L, wherein L denotes halogen, a cyano or nitro group or an alkyl, alkyloxy or alkanoyl group having 1 to 7 C atoms wherein one or more H atoms may be substituted by F or Cl, and Cyc is 1,4-cyclohexylene. Z in these groups, unless otherwise indicated, has the meaning given in formula I as described above and below. The group of preferred mesogenic groups of formula II is comprising the formula II-1 to II-24 as well as their mirror images

	-Phe-Z-Phe-	II-1
	-Phe-Z-Cyc-	II-2
	-Cyc-Z-Cyc-	II-3
5	-PheL-Z-Phe-	II-4
	-PheL-Z-Cyc-	II-5
	-PheL-Z-PheL-	II-6
	-Phe-Z-Phe-Z-Phe-	II-7
	-Phe-Z-Phe-Z-Cyc-	II-8
10	-Phe-Z-Cyc-Z-Phe-	II-9
	-Cyc-Z-Phe-Z-Cyc-	II-10
	-Phe-Z-Cyc-Z-Cyc-	II-11
	-Cyc-Z-Cyc-Z-Cyc-	II-12
	-Phe-Z-Phe-Z-PheL-	II-13
15	-Phe-Z-PheL-Z-Phe-	II-14
	-PheL-Z-Phe-Z-PheL-	II-15
	-PheL-Z-PheL-Z-Phe-	II-16
	-PheL-Z-PheL-Z-PheL-	II-17
	-Phe-Z-PheL-Z-Cyc-	II-18
20	-Phe-Z-Cyc-Z-PheL-	II-19
	-Cyc-Z-Phe-Z-PheL-	II-20
	-PheL-Z-Cyc-Z-PheL-	II-21
	-PheL-Z-PheL-Z-Cyc-	II-22
	-PheL-Z-Cyc-Z-Cyc-	II-23
25	-Cyc-Z-PheL-Z-Cyc-	II-24

In the formulae II-1 to II-24, Z is preferably an ester group (-CO-O- or -O-CO-), -CH₂CH₂- or a single bond.

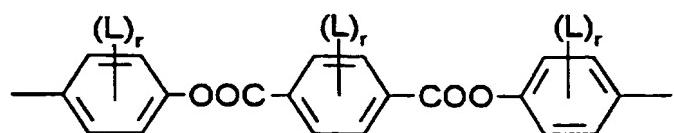
- 30 L in these preferred formulae is preferably F, Cl, CN, NO₂, CH₃, C₂H₅, OCH₃, OC₂H₅, COCH₃, COC₂H₅, CF₃, OCF₃, OCHF₂, OC₂F₅, in particular F, Cl, CN, CH₃, C₂H₅, OCH₃, COCH₃ and OCF₃, most preferably F, Cl, CH₃, OCH₃ and COCH₃.
- 35 Particularly preferably MG, MG*, MG¹ and MG² are selected from the following formulae including their mirror images





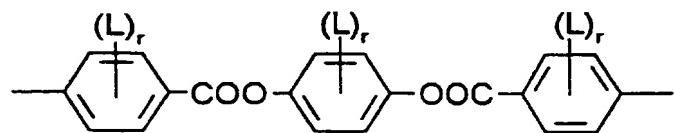
III

5



IIk

10



IIIm

wherein L has the meaning given above and r is 0, 1 or 2.

15

The group in these preferred formulae is very preferably

20

denoting or . furthermore .

with L having each independently one of the meanings given above.

25

In the achiral polymerizable mesogenic compounds of the formula I, R is preferably an achiral alkyl radical which is unsubstituted or substituted by at least one halogen atom, it being possible for one or two non-adjacent CH₂ groups of these radicals to be replaced by -O-, -S-, O-CO-, -CO-O- or -O-CO-O- groups.

30

Halogen is preferably F or Cl.

35

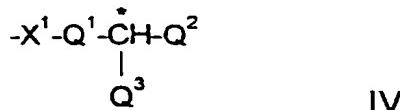
If R is an alkyl or alkoxy radical, i.e. where the terminal CH₂ group is replaced by -O-, this may be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, or octoxy, furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl,

tetradecyl, pentadecyl, methoxy, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy, for example.

5 Oxaalkyl, i.e. where one CH₂ group is replaced by -O-, is preferably straight-chain 2-oxapropyl (=methoxymethyl), 2- (=ethoxymethyl) or 3-oxabutyl (=2-methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, for example.

10 In the polymerizable mesogenic compounds of formula III R* may be an achiral or a chiral group. In case of an achiral group R* preferably has one the preferred meanings given for R above. In case of a chiral group R* is preferably selected according to the following formula IV:

15



20 wherein

X¹ has the meaning given for X,

25 Q¹ is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond,

30 Q² is an alkyl or alkoxy group with 1 to 10 C atoms which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -C≡C-, -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO- or -CO-S- in such a manner that oxygen atoms are not linked directly to one another, or alternatively has the meaning given for P-Sp-,

35

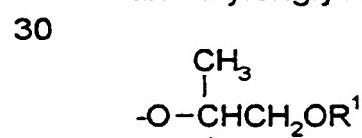
Q^3 is halogen, a cyano group or an alkyl or alkoxy group with 1 to 4 C atoms different from Q^2 .

Preferred chiral groups R^* are 2-butyl (=1-methylpropyl), 2-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, 2-octyl, in particular 2-methylbutyl, 2-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy, 2-octyloxy, 2-oxa-3-methylbutyl, 3-oxa-4-methylpentyl, 4-methylhexyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-methoxyoctoxy, 6-methyloctoxy, 6-methyloctanoyloxy, 5-methylheptyloxy carbonyl, 2-methylbutyryloxy, 3-methylvaleroxyloxy, 4-methylhexanoyloxy, 2-chloropropionyloxy, 2-chloro-3-methylbutyryloxy, 2-chloro-4-methylvaleryloxy, 2-chloro-3-methylvaleryloxy, 2-methyl-3-oxapentyl, 2-methyl-3-oxahexyl, 1-methoxypropyl-2-oxy, 1-ethoxypropyl-2-oxy, 1-propoxypipyl-2-oxy, 1-butoxypropyl-2-oxy, 2-fluoroctyloxy, 2-fluorodecyloxy, for example.

In addition, mesogenic compounds of the formula I and/ or III containing an achiral branched group R or R^* respectively may occasionally be of importance as comonomers, for example, due to a reduction in the tendency towards crystallization. Branched groups of this type generally do not contain more than one chain branch. Preferred achiral branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl (=3-methylbutyl), isopropoxy, 2-methylpropxy and 3-methylbutoxy.

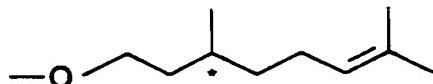
In another preferred embodiment R^* in formula III is denoting a chiral group that is selected from the following groups:

an ethylenglycol derivative



wherein R^1 is an alkyl radical with 1 to 12 C atoms,

35 or a group based on citronellol



5 In another preferred embodiment of the present invention the compounds of formula III comprise a mesogenic or mesogenity supporting group MG* having at least one center of chirality. In these compounds MG* is preferably selected according to formula II*A or II*B:

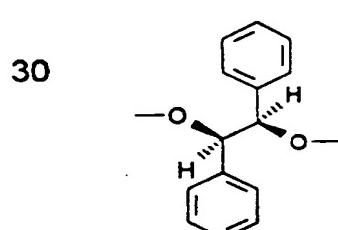
10 $-(A^1-Z)_a-G^1$ II*A

$-(A^1-Z)_a-G^2-(Z-A^2)_b-R$ II*B

15 wherein A^1 , A^2 and Z have the meaning given in formula II, R has the meaning given in formula I, a and b are independently of each other 0, 1 or 2, and

20 G^1 is a terminal chiral group, such as for example a cholesteryl group, a terpenoid radical like e.g. disclosed in the WO 96/17901, particularly preferably a menthyl group, or a terminal chiral sugar derivative comprising a mono- or dicyclic radical with pyranose or furanose rings like, for example, a terminal group derived from the chiral sugars or sugar derivatives as disclosed e.g. in the international application WO 95/16007,

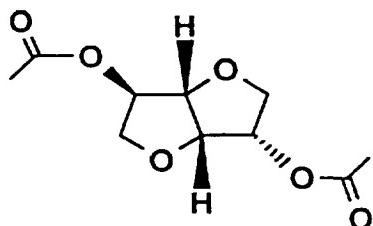
25 and G^2 is a bivalent chiral group, like for example a (R,R)- or (S,S) hydrobenzoin group



or a bivalent chiral sugar, sugar derivative or another bivalent chiral radical, as disclosed e.g. in the international application WO 95/16007, especially preferably a group based on 1,4:3,6-Dianhydro-D-sorbitol:

5

10



15

In case G² is a group based on 1,4:3,6-Dianhydro-D-sorbitol as disclosed above, Z is preferably denoting -CH=CH-.

15

In the compounds of formula I and III P is denoting WHC—O—CH—, CH₂=CW-COO, WCH=CH-O- or CH₂=CH-Phenyl-(O)_k- with W being H, CH₃ or Cl and k being 0 or 1.

20

Preferably P is a vinyl group, an acrylate or methacrylate group, a propenyl ether group or an epoxy group. Especially preferably P is an acrylate or methacrylate group.

25

The polymerizable mesogenic compounds have up to four, in particular up to three, very preferably one or two polymerizable groups.

30

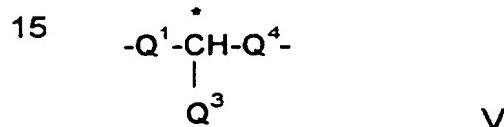
As for the spacer groups Sp and Sp* all groups can be used that are known for this purpose to the skilled in the art. The spacer is preferably linked to the polymerizable group P by an ester or ether group or a single bond. The spacer is preferably a linear or branched alkylene group having 1 to 20 C atoms, in particular 1 to 12 C atoms, in which, in addition, one or more, non-adjacent CH₂ groups may be replaced by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -O-CO-, -S-CO-, -O-COO-, -CO-S-, -CO-O-, -CH(halogen)-, -CH(CN)-, -CH=CH- or -C≡C-.

35

Typical spacer groups are for example $-(CH_2)_o-$, $-(CH_2CH_2O)_r-$, $-CH_2CH_2-$, $-CH_2CH_2-S-CH_2CH_2-$ or $-CH_2CH_2-NH-CH_2CH_2-$, with o being an integer from 2 to 12 and r being an integer from 1 to 3.

5 Preferred spacer groups are ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, ethyleneoxyethylene, methyleneoxybutylene, ethylene-thioethylene, ethylene-N-methyl-iminoethylene and 1-methylalkylene, for example.

10 In a preferred embodiment of the invention the polymerizable mesogenic compounds of formula III comprise a spacer group Sp^* that is a chiral group of the formula V:



wherein

20 Q^1 and Q^3 have the meanings given in formula IV, and

Q^4 is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond, being different from Q^1 .

25 Further preferred are chiral spacer groups Sp^* based on naturally available materials, such as e.g. citronellol or lactate derivatives.

30 In particular preferred are compounds of formula I and/or III wherein n is 1.

In another preferred embodiment, the inventive reflective polarizer is obtained by copolymerizing mixtures comprising compounds of formula I and /or formula III wherein n is 0 and compounds of formula I and/or formula III wherein n is 1.

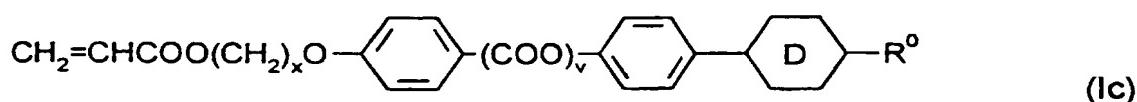
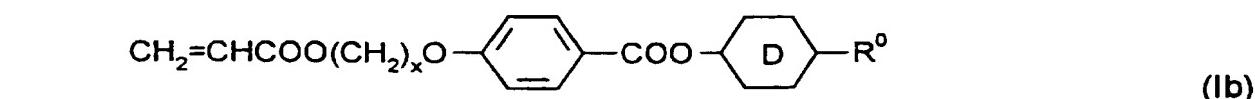
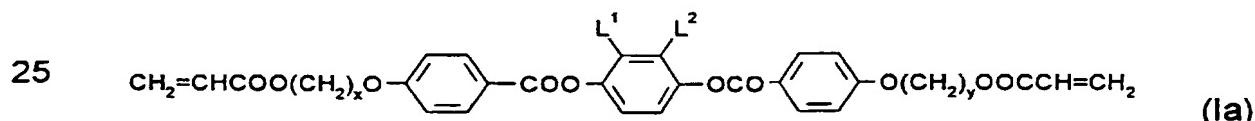
In the event that R, R^{*} or Q² is a group of formula P-Sp-X- or P-Sp*-X- respectively, the spacer groups on each side of the mesogenic core may be identical or different.

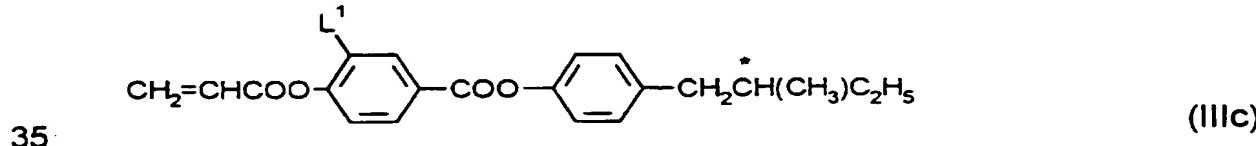
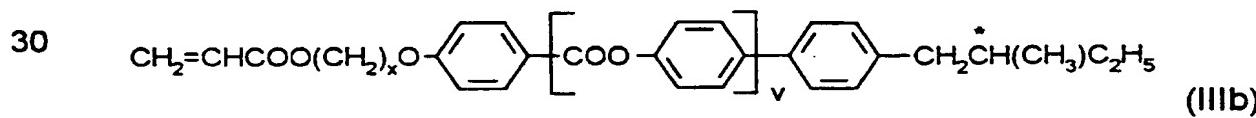
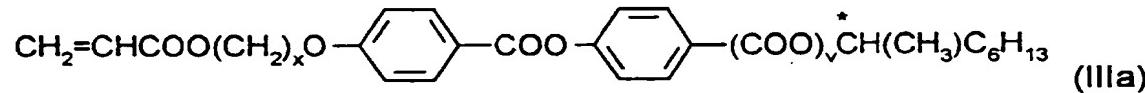
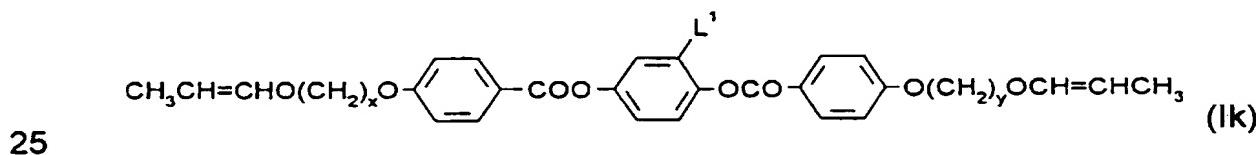
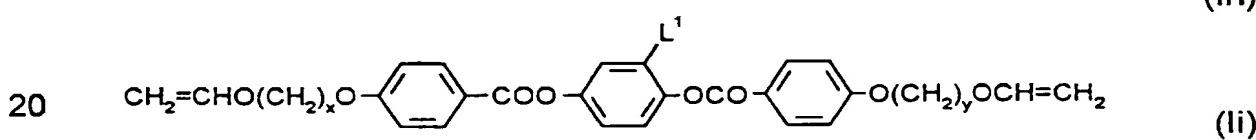
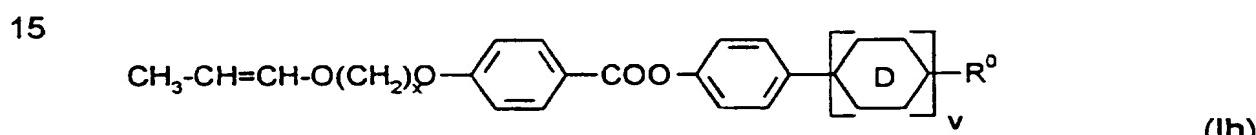
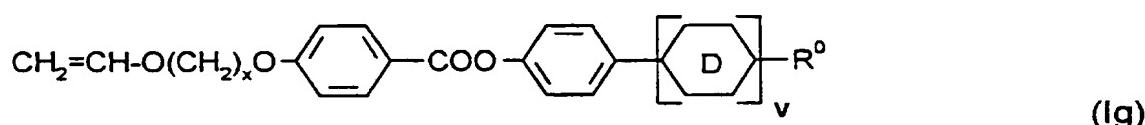
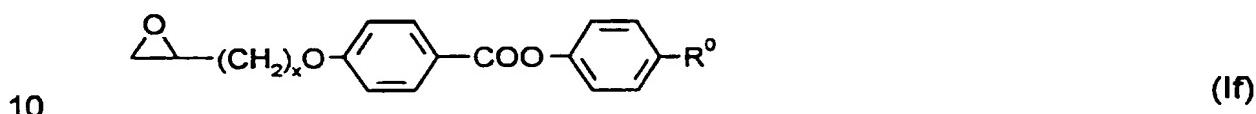
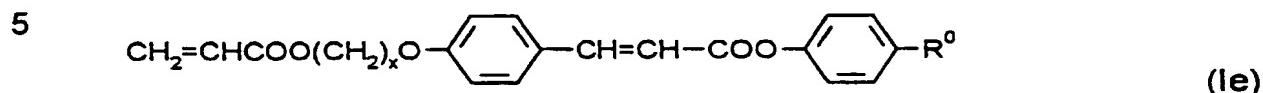
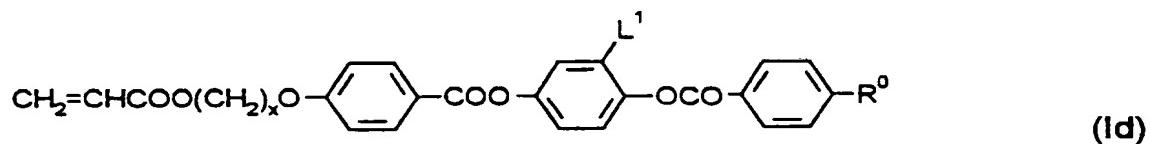
- 5 The polymerizable mesogenic compounds of formula I and III and the non-polymerizable compounds of formula VI can be prepared by methods which are known per se and which are described, for example, in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie,
 10 Thieme-Verlag, Stuttgart. Some specific methods of preparation can be taken from the examples.

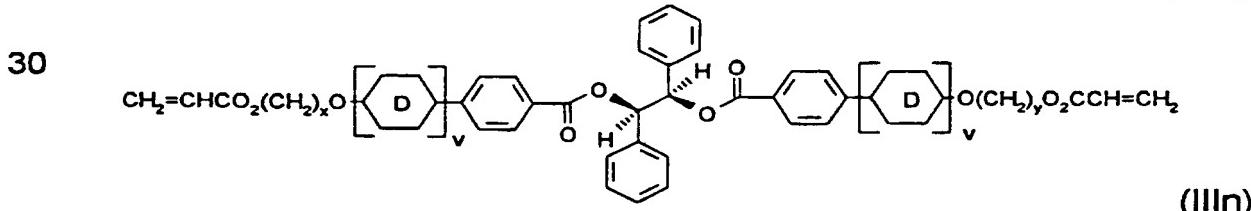
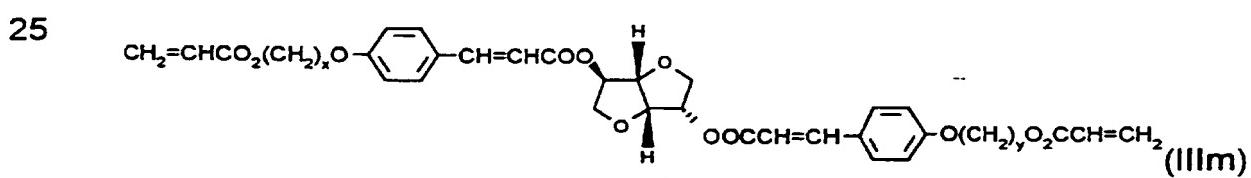
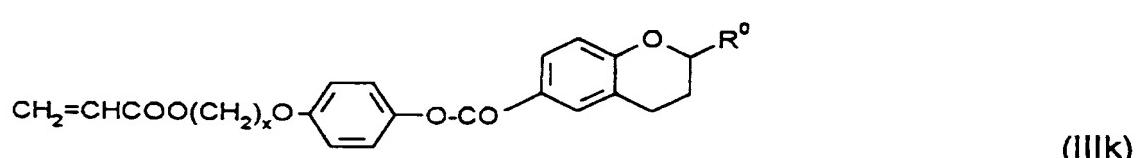
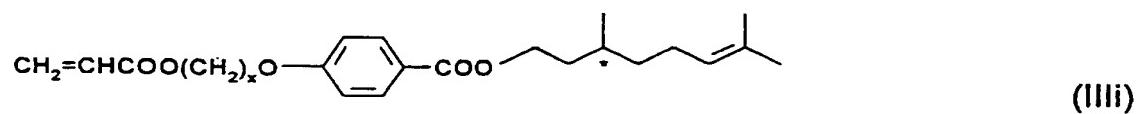
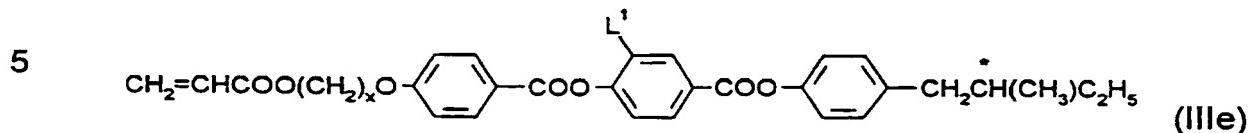
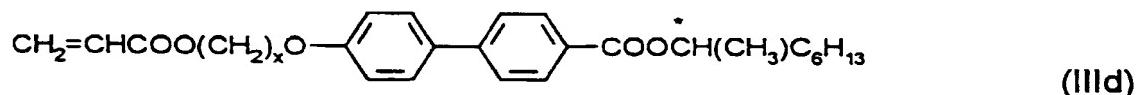
Polymerizable mesogenic compounds according to formula I and III are described for example in WO 93/22397; EP 0 261 712; DE

- 15 19504224; DE 4408171 and DE 4405316. The compounds disclosed in these documents, however, are to be regarded merely as examples that should not limit the scope of this invention.

- 20 Examples representing polymerizable mesogenic compounds of formula I and III are shown in the following list of compounds, which should, however, be taken only as illustrative and is in no way intended to restrict, but instead to explain the present invention:







35 wherein x and y are each independently 1 to 12, v is 0 or 1, D is a 1,4-cyclohexylene or an optionally halogenated 1,4-phenylene group,

T is a terpenoid radical like e.g. menthyl, Ch is a cholesteryl group, R⁰ is halogen, cyano or a chiral or achiral alkyl or alkoxy group with 1 to 12 C atoms and L¹ and L² are each independently H, halogen, CN, or an alkyl, alkoxy or alkanoyl group with 1 to 7 C atoms.

5

In a preferred embodiment of the present invention the achiral polymerizable compounds of formula I are selected of the above formulae Ia to Ik wherein R⁰ is an achiral group.

10

In another preferred embodiment of the present invention the chiral polymerizable compounds of formula III are selected of the above formulae IIIa to IIIm or of formula Ib to Ih wherein R⁰ is a chiral group.

15

In another preferred embodiment of the present invention, component b) of the thermochromic polymerizable mesogenic material is essentially consisting of non-polymerizable chiral mesogenic compounds such as e.g. chiral dopants like those mentioned above. Particularly preferably non-polymerizable chiral compounds are used that comprise at least one chiral group Sp*, MG* and/or R* as given in formula III.

20

Preferably the non-polymerizable chiral mesogenic compounds are selected of formula VI

25

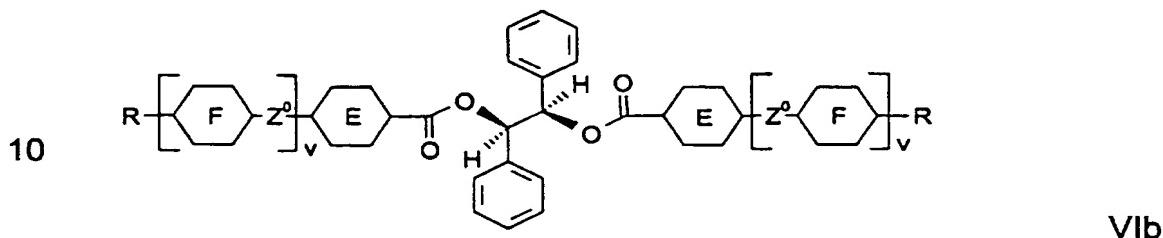
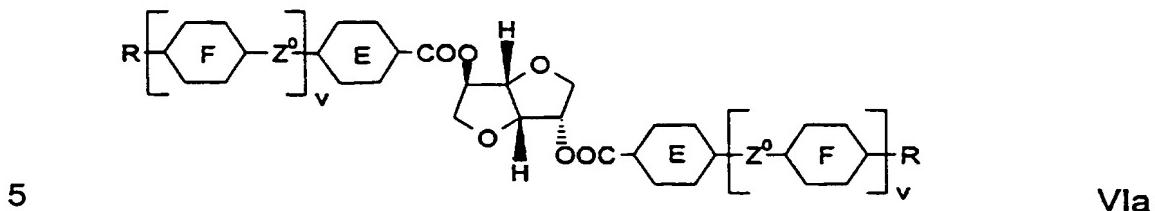
R¹-MG¹-G²-MG²-R² VI

30

wherein MG¹ and MG² each independently have one of the meanings of MG in formula II, R¹ and R² are each independently halogen, cyano or an optionally halogenated alkyl, alkenyl, alkoxy or alkanoyl group with 1 to 12 C atoms, and G² has the meaning of formula II*B. Very preferably G² is a chiral bivalent structure element based on a sugar molecule.

35

In another preferred embodiment of the present invention the chiral non-polymerizable compounds are selected from the following formulae



15 wherein E and F are each independently 1,4-phenylene or trans-1,4-cyclohexylene, v is 0 or 1, Z^0 is $-COO-$, $-OCO-$, $-CH_2CH_2-$ or a single bond, and R is alkyl, alkoxy or alkanoyl with 1 to 12 C atoms.

20 The compounds of formula VIa and their synthesis are described in the international application WO 98/00428, the entire disclosure of which is incorporated into this application by way of reference.

25 Preferred embodiments of the invention are relating to a reflective polarizer as described in the foregoing and the following that is obtainable by copolymerization of one of the following mixtures of a thermochromic polymerizable mesogenic material:

- I) A mixture essentially consisting of
 - a1) 10 to 85 %, preferably 15 to 70 %, in particular 20 to 60 % by weight of at least one achiral polymerizable mesogenic compound according to formula I having one polymerizable group,
 - a2) 0 to 70 %, preferably 0 to 55 %, in particular 0 to 40 % by weight of at least one achiral polymerizable mesogenic

compound according to formula I having two or more polymerizable groups,

5 b1) 5 to 75 %, preferably 10 to 65 %, in particular 15 to 60 % by weight of at least one chiral polymerizable mesogenic compound according to formula III having one polymerizable group,

10 c) 0.01 to 5 % by weight of a photoinitiator.

II) A mixture essentially consisting of

15 a1) 10 to 85 %, preferably 15 to 75 %, in particular 20 to 65 % by weight of at least one achiral polymerizable mesogenic compound having one polymerizable group,

20 a2) 0 to 70 %, preferably 0 to 55 %, in particular 0 to 40 % by weight of at least one achiral polymerizable mesogenic compound having two or more polymerizable groups,

b2) 0.1 to 15 %, preferably 0.2 to 10 %, in particular 0.5 to 5 % by weight of one or more chiral non-polymerizable compounds of formula VI,

25 c) 0.01 to 5 % by weight of a photoinitiator.

and optionally also comprising component b1) in the concentration ranges as described above.

30 Mixtures according to these particularly preferred embodiments are preferred that comprise

- one to five, in particular one to three compounds of component a1) and one or two compounds of component a2).

35 • two to six, in particular two to four different compounds of component a1) and no compounds of component a2).

- one to six, in particular two to four compounds of component a1), one or two compounds of component a2) and one to four, in particular one, two or three compounds of component b1)
- 5 • 2 to 70 %, preferably 3 to 50 %, in particular 5 to 35 % by weight of at least one non-mesogenic compound having two or more polymerizable groups in addition or alternatively to component a2).
- one or two compounds of formula III having two polymerizable groups in addition or alternatively to the components a2) and/or b1).
- 10 • less than 10 % by weight, very especially preferably none of the compounds having two or more polymerizable groups.
- no chiral polymerizable compounds.
- 15 • 0.1 to 20 %, preferably 0.2 to 10 %, in particular 0.5 to 5 % by weight of at least one non-polymerizable chiral compound, like e.g. a chiral dopant, that can also be mesogenic, alternatively or in addition to the components b1) and b2).
- In the mixtures comprising two or more different compounds of formula I and III having one polymerizable group, preferably each of the compounds is different in at least one of the groups P, Sp, X, MG, Sp*, MG*, R or R* from each other of the compounds of the same component.
- 25 The polymerizable compounds of formula I and III in the mixtures according to the preferred embodiments described above are preferably selected of the preferred formulae Ia to Ik and IIIa to IIIm.
- The preferred mixtures described above are another object of the present invention.
- 30 In order to exhibit thermochromic behaviour, the polymerizable compositions used in the present invention have to exhibit a chiral mesophase, like e.g. a chiral smectic or chiral nematic (= cholesteric) liquid crystal phase with a helically twisted molecular structure. Furthermore, the thermochromic polymerizable compositions
- 35

according to the present invention are preferably aligned in a uniform planar orientation, i.e. with the axes of the molecular helices extending substantially normal to the plane of the layer.

- 5 Especially preferred are thermochromic polymerizable compositions having a cholesteric phase. Of these preferred compositions, further preferred are those having a cholesteric phase and additionally a smectic phase at temperatures below the temperature range of the cholesteric phase.

10

The thermochromic compositions can show positive temperature dependency of the pitch, i.e. the pitch increases with increasing temperature, or alternatively they can exhibit negative temperature dependency, i.e. the pitch decreases with increasing temperature.

15

In a preferred embodiment of the present invention the thermochromic polymerizable mesogenic composition exhibits a chiral mesophase with negative temperature dependency of the pitch.

20

In another preferred embodiment of the present invention the thermochromic polymerizable mesogenic composition exhibits a chiral mesophase with positive temperature dependency of the pitch.

25

Since the pitch p is directly related to the reflected wavelength λ and the average refractive index n of the composition by the equation

$$\lambda = n \cdot p$$

30

upon heating or cooling of such a thermochromic composition in its chiral mesophase one can observe a shift of the maximum of the wavelengths reflected by said composition to higher or lower values.

In case the reflection maximum of the composition is in the visible range of light, a colour change of the thermochromic composition upon heating or cooling within its chiral mesophase is observed.

35

According to the above described process of preparing an inventive reflective polarizer, a mixture of a thermochromic polymerizable mesogenic material is coated on a substrate or between two substrates, aligned into a uniform planar orientation and cured by exposure to heat or actinic radiation in the presence of an initiator.

5 A detailed description of this method can be found e.g. in D.J.Broer et al., Makromol.Chem. 190, pp. 2255 ff. (1989).

10 As substrates for example a glass quartz sheet as well as plastic films or sheets can be used.

15 Isotropic or birefringent substrates can be used. In case the substrate is not removed from the polymerized film after polymerization, preferably isotropic substrates are used.

20 In particular for mass production it is suitable to use plastic films as substrates, like e.g. polyester films such as polyethylene-terephthalate (PET), polyvinylalcohol (PVA), polycarbonate (PC) , di- or triacetylcellulose (DAC/TAC). As a birefringent substrate for example an uniaxially stretched plastic film can be used. Preferably at least one substrate is a plastic substrate, especially preferably a PET film or a TAC film. PET films are commercially available e.g. from ICI Corp. under the trade name Melinex.

25 The substrates can be removed after polymerization or not. At least one substrate has to be transmissive for the actinic radiation used for the polymerization.

30 The polymerizable mesogenic material is coated on the substrate or between the substrates in form of a thin layer. This can be done by conventional techniques that are known to the person skilled in the art.

35 It is also possible to dissolve the polymerizable mesogenic material in a suitable solvent. This solution is then coated onto the substrate and the solvent is evaporated off before curing.

- For this purpose, for example standard organic solvents can be used, such as ketones like e.g. methyl ethyl ketone or cyclohexanone, aromatic solvents like e.g. toluene or xylene, halogenated
- 5 hydrocarbons like e.g. di- or trichloromethane, or alcohols such as e.g. methanol, ethanol or isopropyl alcohol. It is also possible to use binary, ternary or higher mixtures of the above solvents.
- The coated layer of the mixture of the thermochromic polymerizable mesogenic material is aligned to give a planar orientation, i.e. wherein the axis of the molecular helix extends transversely to the layer.
- 10 A planar orientation can be achieved for example by shearing the material, e.g. by means of a doctor blade. It is also possible to apply an alignment layer, for example a layer of rubbed polyimide or sputtered SiO_x , on top of at least one of the substrates.
- 15 In another preferred embodiment, the shearing caused by putting together two substrates is sufficient to give good alignment.
- 20 Polymerization of the polymerizable material takes place by exposing it to heat or actinic radiation. Actinic radiation means irradiation with light, like UV light, IR light or visible light, irradiation with X-rays or gamma rays or irradiation with high energy particles,
- 25 such as ions or electrons. Preferably polymerization is carried out by UV irradiation.
- As a source for actinic radiation for example a single UV lamp or a set of UV lamps can be used. Another possible source for actinic radiation is a laser, like e.g. a UV laser, an IR laser or a visible laser.
- 30 For mass production short curing times of 20 minutes or less, very preferably of 8 minutes or less, in particular 5 minutes or less are preferred.
- 35

- The polymerization is carried out in the presence of an initiator absorbing at the wavelength of the actinic radiation. For example, when polymerizing by means of UV light, a photoinitiator can be used that decomposes under UV irradiation to produce free radicals or ions that start the polymerization reaction.
- When curing polymerizable mesogens with acrylate or methacrylate groups, preferably a radical photoinitiator is used, when curing polymerizable mesogens vinyl and epoxide groups, preferably a cationic photoinitiator is used.
- It is also possible to use a polymerization initiator that decomposes when heated to produce free radicals or ions that start the polymerization.
- As a photoinitiator for radical polymerization for example the commercially available Irgacure 651, Irgacure 184, Darocure 1173 or Darocure 4205 (all from Ciba Geigy AG) can be used, whereas in case of cationic photopolymerization the commercially available UVI 6974 (Union Carbide) can be used.
- The thermochromic polymerizable mesogenic material preferably comprises 0.01 to 10 %, very preferably 0.05 to 5 %, in particular 0.1 to 3 % of a polymerization initiator. UV photoinitiators are preferred, in particular radicalic UV photoinitiators.
- In some cases a second substrate is used that does not only aid alignment of the polymerizable composition, but also excludes oxygen that may inhibit the polymerization. Alternatively the curing can be carried out under an atmosphere of inert gas. However, curing in air is also possible using suitable photoinitiators and high lamp power. When using a cationic photoinitiator oxygen exclusion most often is not needed, but water should be excluded.

In a preferred embodiment of the invention the polymerization of the polymerizable composition is carried out under an atmosphere of inert gas, preferably under a nitrogen atmosphere.

- 5 In addition to the polymerization initiators mentioned above, the polymerizable mixture may also comprise one or more other suitable components such as, for example, catalysts, stabilizers, chain-transfer agents, co-reacting monomers or surface-active compounds.
- 10 In a preferred embodiment of the invention, the polymerizable mixture comprises a stabilizer that is used to prevent undesired spontaneous polymerization for example during storage of the composition. As stabilizers in principal all compounds can be used that are known to the skilled in the art for this purpose. These
- 15 compounds are commercially available in a broad variety. Typical examples for stabilizers are 4-ethoxyphenol or butylated hydroxytoluene (BHT). The amount of the stabilizer in the polymerizable mixture is preferably from 1 to 1000 ppm, especially preferably from 10 to 500 ppm.
- 20 Other additives, like e.g. chain transfer agents, can also be added to the polymerizable mixture in order to modify the physical properties of the resulting polymer film. For example when adding a chain transfer agent to the polymerizable mixture, the length of the free
- 25 polymer chains and/or the length of the polymer chains between two crosslinks in the inventive polymer film can be controlled. When the amount of the chain transfer agent is increased, polymer films with decreasing polymer chain length are obtained.
- 30 In a preferred embodiment of the present invention the polymerizable mixture comprises 0.01 to 15 %, in particular 0.1 to 10 %, very preferably 0.5 to 5 % of a chain transfer agent. The polymer films according to this preferred embodiment show especially good adhesion to a substrate, in particular to a plastic film, like e.g. a TAC film. Furthermore, by using polymerizable mesogenic mixtures

comprising a chain transfer agent a reflective polarizer with increased bandwidth can be obtained.

5 As a chain transfer agent for example monofunctional thiol compounds like e.g. dodecane thiol or multifunctional thiol compounds like e.g. trimethylpropane tri(3-mercaptopropionate) can be used.

10 To obtain polymer films with the desired helically twisted planar molecular structure with a good orientation the polymerization has to be carried out in the liquid crystal phase of the polymerizable mesogenic mixture. Therefore preferably polymerizable mesogenic mixtures with low melting points and broad liquid crystal phase ranges are preferred. The use of such mixtures allows to reduce the polymerization temperature, which makes the polymerization process easier and is of importance especially for mass production. 15 Polymerization temperatures below 120 °C are preferred. Especially preferred are temperatures below 90 °C.

20 The thickness of the polymer film influences the bandwidth of the reflective polarizer. Depending on the band position and the bandwidth, the thickness is preferably from 5 to 30 µm. For bandwidths of about 300 nm or more, a thickness of 10 to 20 µm is particularly preferred.

25 In a preferred embodiment the polymerizable mixture additionally contains 0 to 20 %, preferably 0.1 to 10 %, in particular 0.5 to 5 % by weight of a dye having an absorption maximum adjusted to the wavelength of the actinic radiation used for polymerization. Preferably, a dye is used whose absorption maximum lies outside 30 the operation wavelength range of the reflective polarizer in order to exclude undesired absorptions during the use of the polarizer.

In another preferred embodiment of the invention the polymerizable mixture contains no dye.

It is also possible, in order to increase crosslinking of the polymers, to add up to 20% of a non mesogenic compound with two or more polymerizable functional groups to the polymerizable mixture alternatively or in addition to the di- or multifunctional polymerizable mesogenic compounds to increase crosslinking of the polymer.

Typical examples for difunctional non mesogenic monomers are alkyldiacrylates or alkyldimethacrylates with alkyl groups of 1 to 20 C atoms. Typical examples for non mesogenic monomers with more than two polymerizable groups are trimethylpropanetrimethacrylate or pentaerythritoltetraacrylate.

In another preferred embodiment the polymerizable mixture comprises up to 70%, preferably 3 to 50 % of a non mesogenic compound with one polymerizable functional group. Typical examples for monofunctional non mesogenic monomers are alkylacrylates or alkylmethacrylates.

It is also possible to add, for example, a quantity of up to 20% by weight of a non polymerizable liquid-crystalline compound to adapt the optical properties of the inventive reflective polarizer.

Apart from the methods and conditions described above, an inventive broadband reflective polarizer can be prepared as described in the international application WO 97/35219, the entire disclosure of which is incorporated into this application by way of reference.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following examples are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever.

In the foregoing and in the following examples, all temperatures are set forth uncorrected in degrees Celsius and unless otherwise

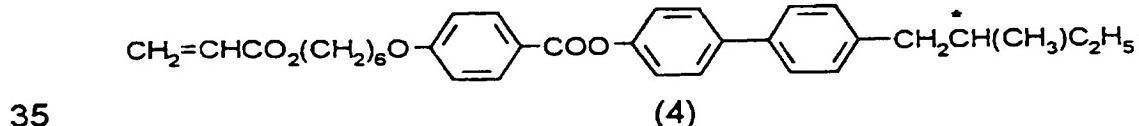
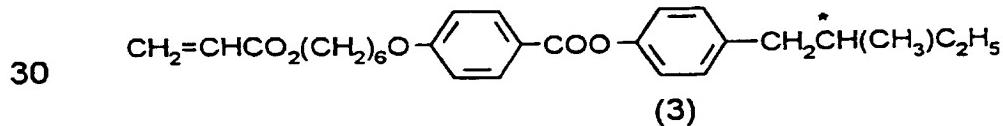
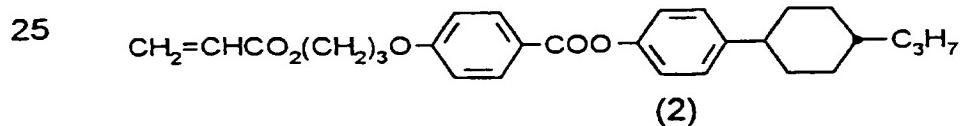
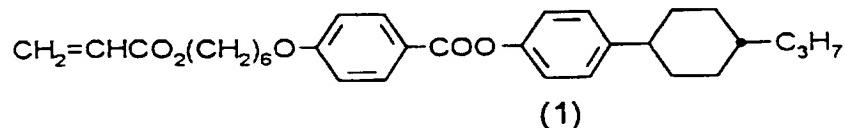
indicated, all parts and percentages are by weight. The following abbreviations are used to illustrate the liquid crystalline phase behaviour of the compounds:

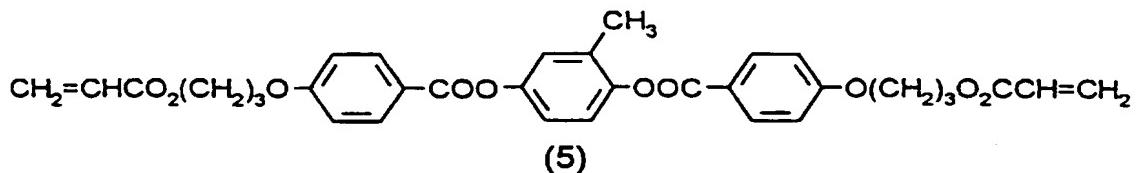
- 5 K = crystalline; N = nematic; S = smectic; Ch = cholesteric; I = isotropic. The numbers between these symbols indicate the phase transition temperatures in degree Celsius.

10 Example 1

The following polymerizable mixture was formulated

	compound (1)	16.5 %
15	compound (2)	11.0 %
	compound (3)	55.0 %
	compound (4)	12.0 %
	compound (5)	5.0 %
20	Irgacure 651	0.5 %





- 5 The compounds (1) and (2) can be prepared as described in the GB 2,280,445 A. The synthesis of compounds (3) and (4) is described in the DE 195,04,224. Compound (5) can be prepared in analogy to the methods described in WO 93/22397.
- 10 Irgacure is a photoinitiator commercially available from Ciba Geigy AG (Basel, Switzerland).
- 15 The mixture shows the liquid crystal phase behaviour S 26.7 Ch 67.2 I, and exhibits the following colour appearance when heated from the smectic phase (the numbers are temperature values in °C):
- 20 Smectic 26.7 Cholesteric Phase, Red 29 Light Green 31 Bright Green 41 Light Blue 50 Deep Blue 59 Violet Blue 67.2 Isotropic Phase.
- 25 The central wavelength of the reflective colour shown by a thin film of this mixture was measured at different temperatures and is shown in **Figure 2**.
- Example 2**
- 30 Thin film samples of the polymerizable mixture of example 1 with a thickness of 5 µm were prepared between two glass slides and heated from 22 °C to 45 °C at a constant rate of 5 °C/min whilst being irradiated with UV light at a range of powers between 0.03 and 0.3 mW/cm².
- 35 In each case there was a time delay before which polymerization occurred in the sample, and this delay was determined by the UV power which the sample received. Once this period was overcome the mixture polymerized rapidly to give a narrow reflecting band.

corresponding to that which was seen in the polymerizable mixture of example 1 at the same temperature, according to **Figure 2**.

5 In this way a range of narrow band reflective films were obtained with the reflective wavelength being depending on the power of UV light supplied as shown in **Figure 3**.

10 This range of powers could then be reproduced within a single film sample by including a UV absorbing dye within the polymerizable mixture to give a gradient of power through the thickness of the film.

Example 3

15 To the polymerizable mixture of example 1 1 % of a UV absorbing dye were added. A sample of the mixture was then prepared as a 15 µm thick film between two glass slides. The sample was irradiated with UV light (0.20 mW/cm^2) at 22°C for 1 min. The sample was then heated from 22°C to 45°C at a constant rate of 10°C/min under 20 continued UV irradiation.

As UV absorbing dye for example the commercially available Tinuvin dyes (from Ciba Geigy) can be used.

25 The transmission spectrum of the polymer film of example 3 was measured and is shown in **Figure 4**, with a) indicating the transmitted and b) the reflected light. The film exhibits a wide reflection waveband between 450 nm and 700 nm and is thus suitable as a broadband reflective polarizer.

30 From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various 35 conditions and usages.

Patent Claims

1. A broadband reflective polarizer comprising a layer of a polymerized mesogenic material exhibiting a helically twisted molecular structure with planar alignment, said reflective polarizer being obtainable by a process wherein a thermochromic polymerizable mesogenic material comprising a mixture of
 - a) at least one achiral polymerizable mesogenic compound,
 - b) at least one chiral compound that can in addition be polymerizable and/or mesogenic,
 - c) a polymerization initiator,
 - d) optionally a dye component,is coated on a substrate or between two substrates in form of a layer, aligned in a planar orientation so that the axis of the molecular helix extends transversely to the layer, and polymerized by exposure to heat or actinic radiation, and optionally the substrates are removed from the polymerized material, characterized in that the temperature is varied during polymerization of the layer of said polymerizable material.
2. A broadband reflective polarizer comprising a layer of a polymerized mesogenic material exhibiting a helically twisted molecular structure with planar alignment, wherein said reflective polarizer is produced by a process wherein a thermochromic polymerizable mesogenic material comprising a mixture of
 - a) at least one achiral polymerizable mesogenic compound,
 - b) at least one chiral compound that can in addition be polymerizable and/or mesogenic,
 - c) a polymerization initiator,
 - f) optionally a dye component,

is coated on a substrate or between two substrates in form of a layer, aligned in a planar orientation so that the axis of the molecular helix extends transversely to the layer, and polymerized by exposure to heat or actinic radiation, and optionally the substrates are removed from the polymerized material, characterized in that the temperature is varied during polymerization of the layer of said polymerizable material.

3. A reflective polarizer according to Claim 1 or 2, wherein the temperature is varied continuously between a minimum value and a maximum value during polymerization.
4. A reflective polarizer according to Claim 1, 2 or 3, wherein at least one of said substrates is a plastic film.
5. A reflective polarizer according to any of Claims 1 to 4, wherein the thermochromic polymerizable mixture comprises a dye component d) for absorbing the actinic radiation used for polymerization.
6. A reflective polarizer according to any of Claims 1 to 5, wherein the reflection characteristics of said reflective polarizer, like the central wavelength, the shape or the bandwidth of the reflected spectrum, are controlled by varying the temperature during polymerisation.
7. A reflective polarizer according to any of Claims 1 to 6, wherein the pitch of the molecular helix varies asymmetrically in the direction normal to the plane of the polarizer.
8. A reflective polarizer according to any of Claims 1 to 7, with a reflection bandwidth of at least 200 nm.
9. A reflective polarizer according to any of Claims 1 to 8, with an asymmetrical pitch structure, wherein the pitch of the molecular

helix substantially increases in a direction normal to the film plane from a smaller value at one side of the film to a higher value at the opposite side of the film.

- 5 10. A reflective polarizer according to any of Claims 1 to 9, wherein the polymerized material forms a three-dimensional network.
- 10 11. A reflective polarizer according to any of Claims 1 to 10, wherein the thermochromic polymerizable mesogenic material contains at least one chiral polymerizable mesogenic compound having one polymerizable group and at least one achiral polymerizable mesogenic compound having one polymerizable group.
- 15 12. A reflective polarizer according to any of Claims 1 to 10, wherein the thermochromic polymerizable mesogenic material contains at least one chiral polymerizable mesogenic compound having one polymerizable group and at least one achiral polymerizable mesogenic compound having two or more polymerizable groups.
- 20 13. A reflective polarizer according to any of Claims 1 to 12, wherein the thermochromic polymerizable mesogenic material contains at least one non-polymerizable chiral compound and at least one achiral polymerizable mesogenic compound having one or two polymerizable groups.
- 25 14. A reflective polarizer, substantially as hereinbefore described, with reference to Examples 1 to 3.
- 30 15. A process of preparing a broadband reflective polarizer comprising a layer of a polymerized mesogenic material exhibiting a helically twisted molecular structure with planar alignment according to any of Claims 1 to 14.
- 35 16. A process of preparing a broadband reflective polarizer according to Claim 15, comprising the steps of coating a

- thermochromic polymerizable mesogenic material comprising
a mixture of
- 5 a) at least one achiral polymerizable mesogenic compound,
 b) at least one chiral compound that can in addition be
 polymerizable and/or mesogenic,
 c) a polymerization initiator,
 d) optionally a dye component,
- 10 on a substrate or between two substrates in form of a layer,
 aligned in a planar orientation so that the axis of the molecular
 helix extends transversely to the layer, polymerizing said
 material by exposure to heat or actinic radiation, and optionally
 removing the substrates from the polymerized material,
 characterized in that the temperature is varied during
 polymerization of the layer of said polymerizable material.
- 15 17. A process of preparing a broadband reflective polarizer
 according to Claim 16, wherein the temperature is varied
 continuously between a minimum value and a maximum value
 during polymerization.
- 20 18. A process of preparing a broadband reflective polarizer
 according to Claim 16 or 17, wherein at least one of said
 substrates is a plastic film.
- 25 19. A process of preparing a broadband reflective polarizer
 according to Claim 16, 17 or 18, wherein the thermochromic
 polymerizable mixture comprises a dye component d) for
 absorbing the actinic radiation used for polymerization.
- 30 20. A process of preparing a broadband reflective polarizer,
 substantially as hereinbefore described, with reference to
 Examples 1 to 3.

21. Use of a broadband reflective polarizer according to any of Claims 1 to 14 in a liquid crystal display.
- 5 22. A liquid crystal display device comprising a liquid crystal cell and a reflective polarizer according to any of Claims 1 to 14, and optionally further comprising at least one of the following components:
 - I) an optical retardation film with a retardation which is approximately 0.25 times the wavelength of the band reflected by the reflective polarizer,
 - 10 II) a linear polarizer,
 - III) a compensation film comprising a layer of an anisotropic polymer material with a homeotropic or tilted homeotropic orientation.
- 15 23. A liquid crystal display device according to Claim 22, comprising the optical elements I, II and optionally also III, wherein the linear polarizer is preferably situated in the optical path between the reflective polarizer and the liquid crystal cell.
- 20 24. A liquid crystal display device according to Claim 22 or 23, comprising the optical elements I, II and optionally also III, wherein the angle between the optical axis of the linear polarizer II and the major optical axis of the optical retardation film I is from 30 degrees to 60 degrees.
- 25



Application No: GB 9820282.3
Claims searched: 1-24

Examiner: Martin Price
Date of search: 27 January 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q): C3P - PDA, PDY, PDZ, PKQ

Int Cl (Ed.6): C09K 19/38; G02B 1/08, 5/30

Other: Online - WPI, EPODOC, PAJ

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X, P	GB 2315760 A	(Merck); polymerisation cannot take place at a completely uniform temperature	1-24
A	EP 0606940 A2	(Philips)	
A, P	WO 97/35219 A1	(Merck)	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.